USE OF COMPOSITE FINGERPRINTS TO DETERMINE THE PROVENANCE OF THE CONTEMPORARY SUSPENDED SEDIMENT LOAD TRANSPORTED BY RIVERS

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ABSTRACT

Sediment fingerprinting appears to offer a valuable alternative to direct monitoring for elucidating the provenance of suspended sediment and the relative importance of spatial zones or subcatchments comprising larger (>500 km^2) drainage basins. Against this background, a quantitative composite fingerprinting technique, incorporating both statistically verified multicomponent signatures and a multivariate sediment-mixing model, has been employed to determine the spatial origin of contemporary suspended sediment transported from the upper and middle reaches of the River Exe (601 km^2) and River Severn (4325 km^2) basins, UK. Spatial origin is addressed in terms of the relative contribution from three distinct geological subareas constituting each study basin. The consistency of the composite fingerprinting approach is examined using the estimates for mean and seasonal variations in source area contributions and also a comparison between the results obtained for individual flood events and alternative lines of evidence provided by flood travel times and the spatial distribution of precipitation. It is argued that fingerprinting estimates for sediment provenance are consistent with existing information on suspended sediment yields from different subcatchments within the study basins, although in the Severn, the role of storage and remobilization in producing signature 'averaging' may complicate comparison of the fingerprinting data with typical floodwater routing times. Validation represents the greatest problem for the cost–benefit of fingerprinting and scope still exists for further refinement of the procedures involved.

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INTRODUCTION

Erosion and sediment yield dynamics have attracted increasing attention from researchers in recent years, since the quest for an improved understanding of the fluvial sediment system now coincides with a number of important environmental concerns and priorities. In particular, information concerning sediment provenance has been identified as an essential prerequisite for elucidating the overall sediment delivery system (Walling, 1990, 1993). Such information has important implications in the design of more effective sediment and pollution control strategies (Wolman, 1977), in the development of more comprehensive sediment budgets and sediment yield models (Campbell *et al*., 1988), in the interpretation of sediment yields in terms of contrasting land management systems in drainage basins (Walling and Woodward, 1992), and in helping to elucidate temporal discontinuities in sediment delivery associated with storage and remobilization phenomena in secondary source areas such as channel and floodplain sinks (Lewin and Macklin, 1987; Droppo and Stone, 1994).

Despite the clear need for sediment provenance data, however, such information has proved difficult to assemble using traditional direct monitoring techniques. Studies employing erosion pins and troughs to estimate soil erosion rates, or sediment load measurements to quantify the relative contribution of suspended sediment from individual sub-basin areas, commonly face important spatial and temporal sampling constraints (Peart and Walling, 1988; Foster *et al*., 1990). Consequently, such approaches are essentially restricted to those investigations of source type undertaken in small-scale (<50 km^2) catchments (e.g. Lewin *et al*., 1974).

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In response to these problems, the use of ‘fingerprinting’ techniques, based on suspended sediment properties, has been shown to afford a valuable and effective alternative approach for establishing sediment sources (Walling and Kane, 1984). Sediment fingerprinting is founded on the premise that spatial and temporal variations in sediment properties directly reflect spatial and temporal variations in the relative contributions of sediment from distinguishable sources. Two basic steps are involved in the application of this approach. The first involves the selection of diagnostic physical and chemical properties which clearly discriminate potential sources in an unequivocal manner. The second involves comparison of the fingerprint properties of the potential sources with the corresponding values for sediment samples in order to establish the relative importance of individual sources.

Traditionally, the search for diagnostic properties has involved the qualitative interpretation of single-component signatures, encompassing an extensive range of mineralogic (Wood, 1978), colorimetric (Grimshaw and Lewin, 1980), mineral–magnetic (Bonnett *et al*., 1989), chemical (Jones *et al*., 1991), organic (Peck, 1973), radiometric (Walling and Woodward, 1992), isotopic (Newman *et al*., 1973) and physical, e.g. absolute particle size (Santiago *et al*., 1992), properties and property ratios. More recently, realization that the search for a single diagnostic property is likely to prove elusive and that spurious source–sediment matches can result from the use of single fingerprint properties, has resulted in the development of composite fingerprinting procedures. These incorporate multicomponent signatures comprising several individual fingerprint properties drawn from either particular property subsets, e.g. radiometric parameters (Oldfield and Clark, 1990; He and Owens, 1995), or from a range of different subsets, e.g. a combination of mineral-magnetic, radiometric and geochemical parameters (Walling *et al*., 1993; Collins, 1995; Walling and Woodward, 1995; Collins *et al*., 1996). The adoption of composite signatures has also been coupled with the development of more rigorous quantitative procedures for sediment fingerprinting, involving both statistical verification of the discrimination provided by particular tracer parameters and the use of multivariate mixing models to establish the relative contributions of individual sources (Yu and Oldfield, 1989, 1993; Shankar *et al*., 1994; Collins, 1995; Walling and Woodward, 1995; Collins *et al*., 1996).

To date, most fingerprinting studies, whether employing qualitative or quantitative methodologies, or single-component or composite signatures, have been primarily concerned with distinguishing *source types* (e.g. surfaces under different land uses and channel banks) within small ($<50\,km^2$) catchments (Walling and Woodward, 1992). Larger basins ($>500\,km^2$), however, generally encompass greater heterogeneity of source material properties, with the result that source type fingerprinting is rendered more difficult and potentially less meaningful. Fingerprinting studies in large catchments have therefore focused primarily on the *spatial provenance* of transported sediment (Caitcheon, 1993a,b; Walling and Woodward, 1995; Collins *et al*., 1996). The fingerprinting of spatial origin is based on the assumption that sediments derived from subareas with contrasting geological or pedological characteristics should exhibit distinctive fingerprints. These fingerprints can then be used to assess the relative contributions of the subareas to the sediment load sampled at a downstream point. However, although such fingerprinting of sediment provenance appears to offer considerable potential for larger river basins, the viability of the approach has not been rigorously tested. This contribution attempts to provide such verification by applying a composite fingerprinting procedure, incorporating both statistically verified multicomponent signatures and a multivariate mixing model, to investigate the spatial origin of suspended sediment (characterized in terms of geologically defined subareas) in the upper and middle reaches of the River Exe ($601\,km^2$) and Severn ($4325\,km^2$) basins, UK. These two basins were selected to afford contrasts in both catchment size and physiographic conditions, thereby providing a meaningful test of the spatial origin fingerprinting approach.

THE STUDY BASINS

The River Exe drainage basin, located in southwest England (see Figure 1), is underlain by Devonian (slates, grits), Carboniferous (shales, sandstones) and Permian (marls, breccias, sandstones) strata (see Figure 2). This geological diversity is closely reflected in the other catchment physiographic characteristics. Elevations associated with the Devonian strata in the north commonly exceed 400 m, but fall to 50–200 m on the Carboniferous and Permian strata to the south. Steep slopes are observed in northern areas (20–30°) underlain

Figure 1. Location of the Exe study basin

by the Devonian rocks, and in southern areas (>11°) where the Carboniferous strata are characterized by deeply dissected terrain. The contrasting altitudes within the Exe basin result in considerable spatial variability in mean annual precipitation. The more elevated northern areas commonly receive almost 1800 mm per annum, whilst the central and southern areas receive almost 1200 mm and 900 mm per annum, respectively. Corresponding spatial variability is observed for runoff, with an annual runoff of 1500 mm in northern areas decreasing to 800 mm for central areas and to 450 mm for southern areas. Pastoral farming dominates the northern areas of the basin, whilst mixed pastoral/arable farming is observed further to the south. Typical annual suspended sediment yields are estimated to be *c*. 16–58 t km^{-2} y^{-1} for various sites within the basin (Walling and Webb, 1987). The flow gauging station at Thorverton was chosen as the basin outlet, yielding a total catchment area of 601 km^2, representing the upper and middle Exe (see Figure 1).

The catchment of the River Severn represents one of the largest drainage basins in the UK (see Figure 3) and is underlain by Precambrian (lavas), Cambrian (shales, sandstones, quartzites), Ordivican (mudstones, shales), Silurian (shales, grits), Devonian (sandstone), Carboniferous (limestones, sandstones), Permo-Triassic (sandstones) and Jurassic (sandstones) strata (see Figure 4). Relief generally decreases from west to east and from north to south, with elevations of 752 m at the source in the northwest falling to 50–200 m in the southeast. Steep slopes (>30°) dominate the western upland areas, whilst further to the east, the Shropshire Plain is characterized by slopes of only 4–6°. Considerable spatial variability is exhibited by mean annual precipitation due to the influence of the western uplands. Western areas commonly receive 2500 mm per annum, which then

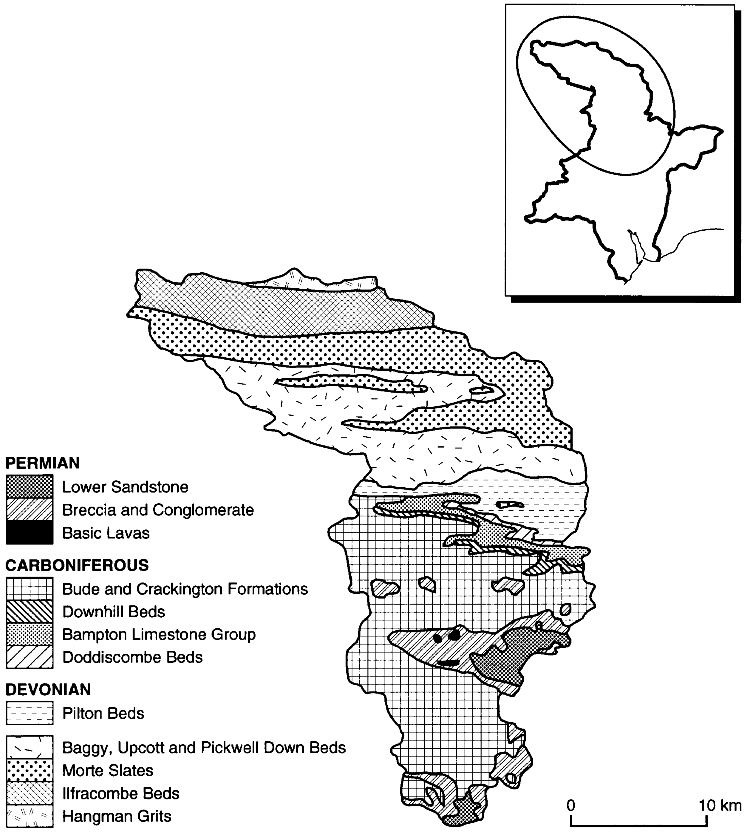

Figure 2. Solid geology of the Exe study basin

declines rapidly to 800 mm per annum in central areas and then 700 mm per annum in eastern areas. Pastoral farming is dominant in western areas, with coniferous forest plantations in some headwaters, whilst arable agriculture is widespread in the east. Typical annual suspended sediment yields are estimated to lie within the range 10–100 t km^{-2} a^{-1} (Walling and Quine, 1993). The flow gauging station at Bewdley was selected as the basin outlet, providing a total catchment area of 4325 km^2, representing the upper and middle Severn (see Figure 3).

FIELD SAMPLING AND LABORATORY PROCEDURES

Field sampling

To permit the provenance of bulk suspended sediment samples collected at the basin outlet to be examined in terms of *geological subareas*, detailed source material sampling was undertaken within each of the major geological systems constituting each study basin. Source material sampling was stratified to encompass both the major land use categories and channel banks, in order to provide representative samples of surface and subsurface materials for each geological system, as opposed to permitting an explicit investigation of sediment source type *per se*.

For the Exe, ten samples of surface soil from woodland, pasture and cultivated areas, and channel bank material, were collected for each individual rock series constituting the three geological systems underlying the study area. This yielded a total of 480 source material samples, i.e. 200, 160 and 120 samples for the Devonian, Carboniferous and Permian systems, respectively. For the Severn, four samples of surface soil from woodland, pasture and cultivated areas, and of channel bank material, were collected for each of the series constituting

Figure 3. Location of the Severn study basin

three grouped geological systems, i.e. the Ordovician–Silurian, Devonian–Carboniferous–Permian, and Triassic–Jurassic systems. This yielded a total of 256 source material samples, i.e. 80, 96 and 80 samples for the three systems, respectively. The remaining geological systems in the Severn basin study area did not represent significant potential sources, as collectively they accounted for only 3·2 per cent of the study area. Care was taken to ensure that source material samples represented either topsoil likely to be eroded (i.e. 0–2 cm depth) from surficial sources, or geological and colluvial material forming actively eroding channel banks. Fewer samples were collected for the Severn basin study area, as this work was undertaken as a reconnaissance survey.

Bulk water samples (50–500 l) were retrieved during flood events at the basin outlets using a submersible pump suspended from a bridge and powered by a portable generator. Because these samples were typically collected over a short duration, they represented essentially instantaneous samples of the suspended sediment load at the time of sampling (Walling and Woodward, 1995). Sample collection encompassed a range of suspended sediment concentrations and anticipated seasonal, inter- and intra-storm variations in sediment properties (cf. Ongley *et al*., 1981; Walling and Woodward, 1992). A total of 42 suspended sediment samples was retrieved from the Thorverton gauging station on the Exe during 15 individual flood events, whilst for the Severn at Bewdley, a total of 23 samples was collected during nine individual flood events. The source material and basin outlet suspended sediment samples pertaining to each study area were then compared using a range of potential fingerprint properties, in order to determine the spatial provenance of the suspended sediment load.

Laboratory analysis of fingerprint properties

All bulk suspended sediment samples collected from the basin outlets were dewatered using an Alfa-Laval continuous-flow centrifuge, and then freeze-dried prior to more detailed laboratory analysis. Source material

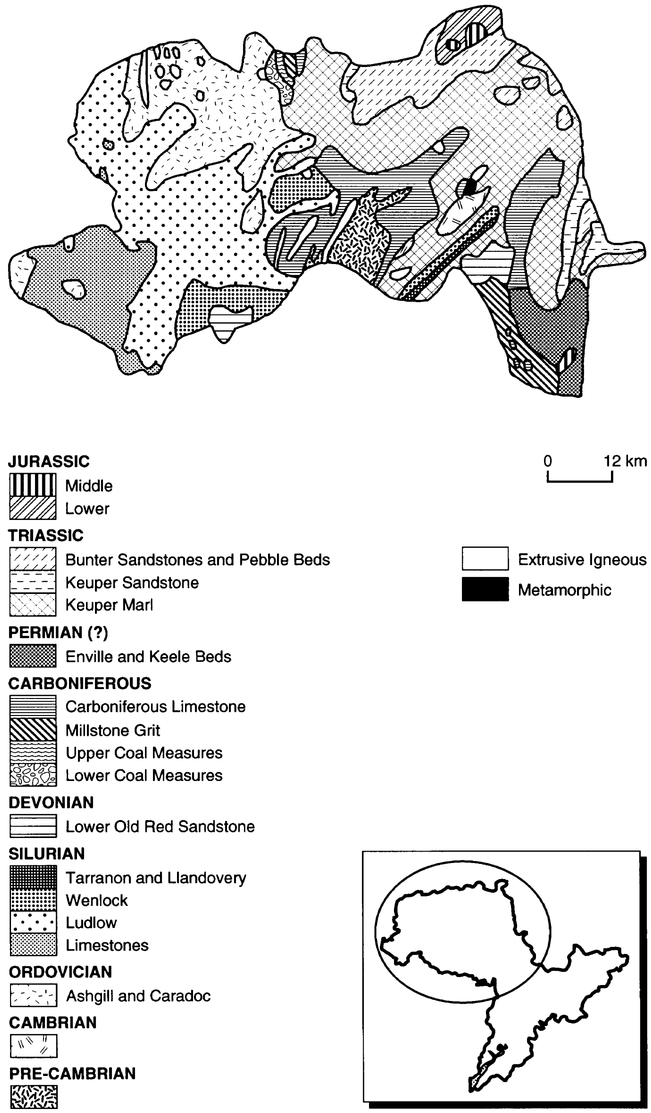

Figure 4. Solid geology of the Severn study basin

samples were air-dried on porous plates, gently disaggregated using a pestle and mortar and then dry-sieved to <63 μm to facilitate direct comparison with sediment samples. To ensure maximum sieving efficiency, sieve loads were minimized, sieving times were standardized and the splitting of samples was avoided (cf. McManus, 1965; Emmerling and Tanner, 1974; Dalsgaard *et al.*, 1991).

Laboratory analysis of both source material and suspended sediment samples was undertaken for a range of potential fingerprint properties comprising several property subsets, i.e. trace metals (Fe, Mn, Al), heavy metals (Cu, Zn, Pb, Cr, Co, Ni), base cations (Na, Mg, Ca, K), other organic and inorganic (C, N, total P) and physical (absolute particle size) parameters. Fe, Mn and Al extraction involved both pyrophosphate–dithionite (Bascomb, 1968) and oxalate (Deb, 1950) methods, whilst extraction of heavy metals involved direct acid digestion (Allen, 1989). Base cation extraction was achieved with the use of acid ammonium acetate (Qui and Zhu, 1993). Extract concentrations were determined using atomic absorption spectrophotometry (AAS) with either an air/acetylene or a nitrous oxide/acetylene flame. Direct determination of C and N was undertaken using a Carlo Erba Elemental Analyser, whilst colorimetric determination of total P was undertaken using UV–

visible spectrophotometry following extraction with perchloric acid (Olsen and Dean, 1965). Absolute particle size composition was determined after sample pretreatment with hydrogen peroxide (McManus, 1988) and sodium hexametaphosphate, using a Malvern Mastersizer.

USE OF COMPOSITE FINGERPRINTS

The composite fingerprinting procedure

The composite fingerprinting procedure used to provide a quantitative assessment of the relative contributions from the geological subareas constituting each study basin, to the sediment load sampled at the corresponding basin outlet, involved two main stages:

(a) use of a statistical verification procedure for individual fingerprint properties to identify a subset of these properties, or composite fingerprint, capable of discriminating subareas of the study basins associated with individual geological types;
(b) application of a multivariate mixing model to these composite fingerprints to provide quantitative estimates of the relative contributions of the different geological subareas to the sampled sediment load.

Discriminating provenance using statistically verified composite signatures

Previous fingerprinting studies have identified the need for statistical verification of tracer parameters, in order to ensure that source area discrimination is accomplished in an unequivocal manner (Walling *et al*., 1993; Walling and Woodward, 1995). With this objective in mind, a two-stage statistical selection procedure was applied to the list of potential fingerprint properties considered in this study, to identify composite signatures capable of distinguishing subareas of the study basins associated with individual geological types. In the case of the River Exe, three subareas representing zones underlain by Devonian, Carboniferous and Permian strata were involved. In the case of the River Severn, three subareas representing zones underlain by Ordovician–Silurian, Devonian–Carboniferous–Permian, and Triassic–Jurassic strata were selected.

In stage one, all individual potential fingerprint properties were tested for their ability to distinguish the subareas representing the main geological systems within each study basin. This was based on all the source material samples for each drainage basin and involved using the non-parametric Kruskal–Wallis H-test. A non-parametric test was used, since analysis of the raw tracer parameter data revealed that the main conditions for adopting a parametric test, i.e. that the data are uniformly distributed and have equal variances, could not be satisfield. Mean fingerprint property values and associated coefficients of variation for each geological subarea, together with the corresponding significance levels for the Kruskal–Wallis test, are presented in Tables I and II. Greater inter-group differences provide larger H-values (Shaw and Wheeler, 1985). The critical H-value (95 per cent significance level) is 5·99 for the Exe and 5·60 for the Severn. For each study basin, all parameters yield H-values in excess of the corresponding critical value and so pass the test. These results confirm that there is a 95 per cent probability that differences between the mean values of these fingerprint properties for each geological subarea are not the result of random variations. Success in the Kruskal–Wallis test was used as a criterion for entering parameters in stage two.

Stage two involved the use of multivariate discriminant function analysis to identify, from the parameters successful in stage one, the composite signatures capable of distinguishing correctly 100 per cent of the source material samples associated with each geological subarea in the two study basins. Composite signatures were selected using the minimization of Wilks' lambda as a stepwise selection algorithm. A lambda of 1 occurs when all group means are equal. Values close to zero occur when within-group variability is small compared to total variability, i.e. when most of the total variability is attributable to differences between the group means. Composite signatures capable of providing comprehensive discrimination of the geological subareas within each study basin will therefore be associated with lower lambda values. Table III presents the final results of the discriminant function analysis for the Exe and Severn basins. Both composite signatures yield lambda values close to zero and comprise individual properties from a range of different subsets. This underscores the need to use a wide range of potential fingerprint properties, preferably with differing environmental behaviour (Walling *et al*., 1993; Collins, 1995; Walling and Woodward, 1995), as opposed to several properties from a

Table I. Kruskal-Wallis H-test significance levels for distinguishing geologicdal subareas in the Exe basin using individual fingerprint properties

Tracer property	Devonian		Carboniferous		Permian		'H' value
	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)	
Pyrophosphate Fe (%)	0·50	5·5	0·24	21·5	0·19	18·5	29·72
Dithionite Fe (%)	0·24	9·9	0·63	21·0	0·70	19·8	22·80
Pyrophosphate Al (%)	0·70	24·9	0·11	23·0	0·02	25·8	33·86
Dithionite Al (%)	0·03	20·5	0·04	24·4	0·02	15·6	12·21
Pyrophosphate Mn (%)	0·03	31·8	0·01	29·8	0·03	22·9	26·20
Dithionite Mn (%)	0·01	20·0	0·04	16·3	0·02	17·9	18·31
Total of pyrophosphate and dithionite Fe (%)	0·74	5·5	0·87	16·8	0·89	16·5	15·53
Total of pyrophosphate and dithionite Al (%)	0·73	21·9	0·15	22·1	0·04	19·8	28·31
Total of pyrophosphate and dithionite Mn (%)	0·04	17·2	0·05	27·5	0·05	26·3	14·12
Oxalate Fe (%)	0·54	27·5	0·70	13·7	0·60	22·3	9·34
Oxalate Mn (%)	0·20	19·3	0·10	21·5	0·14	16·6	11·80
Oxalate Al (%)	–	–	–	–	–	–	–
Cu (mg kg^{-1})	70·00	20·4	50·25	20·8	138·75	23·4	29·27
Zn (mg kg^{-1})	29·00	11·6	38·00	16·5	185·00	10·5	31·10
Pb (mg kg^{-1})	23·25	22·9	57·60	16·0	64·75	13·2	35·81
Cr (mg kg^{-1})	20·00	12·3	29·25	11·7	27·50	27·5	26·38
Co (mg kg^{-1})	15·40	16·6	20·00	19·3	19·80	11·0	27·53
Ni (mg kg^{-1})	21·80	24·0	27·00	27·3	32·00	18·8	12·30
Na (mg kg^{-1})	9·01	29·3	23·42	12·0	7·99	23·0	19·91
Mg (mg kg^{-1})	2·06	18·1	44·13	22·1	35·02	23·1	30·79
Ca (mg kg^{-1})	35·71	12·4	42·33	29·0	70·41	19·0	33·64
K (mg kg^{-1})	3·56	29·5	2·04	19·6	3·58	15·7	13·73
Total P (%)	0·05	8·0	0·01	11·5	0·10	14·4	26·39
C (%)	12·55	16·0	2·73	22·0	3·21	19·1	9·59
N (%)	0·87	15·3	0·93	28·3	0·99	21·0	9·27

Critical H-value at 0·05 = 5·99

Table II. Kruskal-Wallis H-test significance levels for distinguishing geological subareas in the Severn basin using individual fingerprint properties

Tracer property	Ordovician-silurian		Devonian-Carboniferous–Permian		Triassic-Jurassic		'H' value
	Mean	CV (%)	Mean	CV (%)	Mean	CV (%)	
Pyrosphate Fe (%)	0·24	6·6	0·27	29·7	0·20	17·5	9·34
Dithionite Fe (%)	0·40	22·5	0·80	21·2	0·52	18·6	14·41
Pyrophosphate Al (%)	0·10	12·5	0·07	22·4	0·15	6·5	16·74
Dithionite Al (%)	0·11	17·5	0·20	13·2	0·10	18·6	15·80
Pyrophosphate Mn (%)	0·04	22·5	0·30	17·1	0·10	24·0	16·96
Dithionite Mn (%)	0·10	13·4	0·97	16·8	0·20	21·8	18·22
Total of pyrophosphate and dithionite Fe (%)	0·64	14·9	1·07	22·0	0·72	14·7	13·24
Total of pyrophosphate and dithionite Al (%)	0·21	10·2	0·27	12·5	0·25	15·5	12·46
Total of pyrophosphate and dithionite Mn (%)	0·14	13·0	1·27	13·1	0·30	22·0	17·43
Oxalate Fe (%)	0·45	14·5	0·62	6·5	0·40	5·6	7·21
Oxalate Mn (%)	0·04	24·0	0·60	18·4	0·21	6·2	18·10
Oxalate Al (%)	0·10	29·4	0·13	24·7	0·06	11·4	15·05
Cu (mg kg^{-1})	32·37	6·5	41·20	23·8	125·00	17·7	11·67
Zn (mg kg^{-1})	127·62	3·7	74·75	18·9	102·12	6·6	16·19
Pb (mg kg^{-1})	55·62	6·7	25·62	15·0	101·30	17·3	12·65
Cr (mg kg^{-1})	32·40	6·5	21·43	9·8	93·75	15·5	15·40
Co (mg kg^{-1})	18·12	10·2	15·00	16·0	24·40	14·3	18·16
Ni (mg kg^{-1})	39·40	13·1	33·80	12·6	22·00	13·0	13·63
Na (mg kg^{-1})	65·62	27·1	13·20	23·6	8·70	17·1	11·55
Mg (mg kg^{-1})	59·90	23·7	76·00	21·0	32·62	22·3	17·93
Ca (mg kg^{-1})	46·00	28·5	90·92	26·0	43·82	7·3	17·45
K (mg kg^{-1})	15·50	16·7	53·42	25·3	31·00	11·0	18·29
Total P (%)	0·01	12·9	0·03	12·5	0·06	23·0	15·01
C (%)	15·28	19·4	12·70	18·1	21·82	14·2	17·50
N (%)	1·02	25·0	0·90	9·5	1·30	8·0	17·71

Critical H-value at 0·05 = 5·60

Table III. Final results of the stepwise discriminant function analysis

	Tracer property	Wilks' lambda	Cumulative % geological type source samples classified correctly
Exe	Total P	0·46190	60·00
	Cu	0·42991	74·17
	Dithionite Mn	0·41886	77·55
	Ni	0·35556	82·33
	Cr	0·30044	85·00
	Zn	0·23222	88·25
	Dithionite Al	0·10000	92·00
	Na	0·00887	93·33
	Mg	0·00569	95·00
	K	0·00046	96·15
	Ca	0·00012	97·88
	Pyrophosphate Al	0·00008	98·50
	Pb	0·00006	99·17
	N	0·00001	100·00
Severn	Cr	0·23499	85·42
	K	0·00229	93·75
	Zn	0·00009	100·00
	Pb	0·00005	100·00
	Total of pyrophosphate and dithionite Al	0·00001	100·00

single subset, e.g. the radiometric subset (He and Owens, 1995), or the mineral–magnetic subset (Slattery *et al*., 1995). Furthermore, although Cr, K and Zn are shown to distinguish correctly 100 per cent of the source material samples used to characterize the three geological subareas in the Severn basin, Pb and the total of pyrophosphate and dithionite Al are also incorporated into the final composite signature, as the additional information provided by these properties will inevitably improve the reliability of the discrimination afforded by the composite fingerprint. This is demonstrated by a continuing decrease in the value of Wilks' lambda (see Table III).

Use of a multivariate sediment-mixing model to establish spatial provenance

On the assumption that fingerprint property concentrations, in any given suspended sediment sample, are dependent upon the corresponding concentrations in the original source material and the relative proportions of such material contributed by different geological subareas constituting that sample, the composite signatures were used with a multivariate sediment-mixing model to establish the relative contribution of the different geological subareas to the suspended sediment sample. The mixing model seeks to satisfy the following constraints.

(a) The contributions of the geological subareas to the suspended sediment load sampled at the corresponding basin outlet must all be non-negative:

$$0 \leq P_g \leq 1 \qquad (1)$$

(b) The contributions of the geological subareas to the suspended sediment load sampled at the corresponding basin outlet must sum to unity:

$$\sum_{g=1}^{n} P_g = 1 \qquad (2)$$

A linear equation (see Equation 3) is established for each property contained within each composite signature. The resultant set of linear equations pertaining to each signature is generally overdetermined, and so optimization of the estimates for the relative contributions from individual geological subareas is achieved by minimizing an objective function represented by the sum of squares of the weighted relative errors:

$$\sum_{i=1}^{n} \left\{(C_i - (P_{g1}S_{ig1}Z_{g1}O_{g1} + P_{g2}S_{ig2}Z_{g2}O_{g2} + P_{g3}S_{ig3}Z_{g3}O_{g3})) / C_i\right\}^2 W_i \quad (3)$$

where Ci = concentration of tracer parameter (i) in basin outlet suspended sediment sample; P_{g1} = percentage contribution from geological subarea g_1; S_{ig1} = mean concentration of tracer parameter (i) in source material samples for geological subarea g_1; Z_{g1} = particle size correction factor (ratio of basin outlet sediment sample specific surface area to mean specific surface area for each geological subarea); O_{g1} = organic matter content correction factor (ratio of basin outlet sediment sample organic carbon content to mean organic carbon content for each geological subarea); W_i = tracer-specific weighting.

The source material tracer data pertaining to each study area are aggregated to provide a single mean value for each geological subarea under scrutiny, which is then used in the mixing model to determine the spatial provenance of individual suspended sediment samples collected at the corresponding basin outlet. Tables I and II demonstrate that the fingerprint property concentrations associated with the individual geological subareas exhibit significant variation, and caution is therefore needed when interpreting the results of the mixing model employed in this study, which are based on the use of mean concentrations. However, it should be recognized that the mean concentration values used for an individual geological subarea effectively represent the concentration associated with the mixture of samples taken from a range of sites within that subarea. It is therefore reasonable to assume that this mean value is directly comparable to the concentration associated with suspended sediment derived from a range of sites within the geological subarea. The inherent variability of the fingerprint properties within the subarea is thus taken into account by comparing a mean value for the source samples with a value for the suspended sediment which reflects a mixture of material from different sites.

Research has demonstrated that particle size exerts an important influence upon element concentrations in soils and sediments (Horowitz and Elrick, 1987). A particle size correction factor Z_{g1} is necessary, therefore, to permit a direct comparison of the fingerprinting properties between materials which possess contrasting particle size characteristics. The correction factor used in this study is based upon specific surface area ($m^{-2}\ g^{-1}$), since this characteristic closely reflects particle size composition (Horowitz, 1991). Specific surface area data were calculated from the Malvern Mastersizer output (assuming sphericity of particles) using the total surface area in each size class divided by the percentage volume of a given sample within that size class (Mastersizer Instruction Manual, 1988). Typical specific surface area values for the geological subarea source samples and suspended sediment samples pertaining to each study basin are presented in Table IV. The ratio of the specific surface area of each individual suspended sediment sample collected at the basin outlets to the mean specific surface area of source material from each geological subarea within the corresponding basin was utilized as a correction factor. This yielded mean particle size correction factors of 1·31 (Devonian), 1·13 (Carboniferous) and 1·10 (Permian) for the Exe and 1·22 (Ordovician–Silurian), 1·20 (Devonian–Carboniferous–Permian) and 1·16 (Triassic–Jurassic) for the Severn. Incorporation of this particle size correction factor into the optimized mixing model ensured comparability of the source material sample fingerprint property concentrations with the suspended sediment sample concentrations.

Table IV. Specific surface area data for the Exe and Severn basins

	Devonian		Carboniferous		Permian		Suspended sediment	
Exe	Mean ($m^{-2}g^{-1}$)	CV (%)	Mean ($m^{-2}g^{-1}$)	CV (%)	Mean ($m^{-2}g^{-1}$)	CV (%)	Mean ($m^{-2}g^{-1}$)	CV (%)
	0·4000	17·0	0·4590	13·2	0·4730	18·3	0·5222	33·1
	Ordovician–Silurian		Devonian–Carboniferous–Permian		Triassic–Jurassic		Suspended sediment	
Severn	Mean ($m^{-2}g^{-1}$)	CV (%)	Mean ($m^{-2}g^{-1}$)	CV (%)	Mean ($m^{-2}g^{-1}$)	CV (%)	Mean ($m^{-2}g^{-1}$)	CV (%)
	0·4825	19·0	0·4925	15·7	0·5094	13·6	0·5910	24·7

Table V. Organic carbon content data for the Exe and Severn basins

Exe	Devonian		Carboniferous		Permian		Suspended sediment	
	Mean (%)	CV (%)	Mean (%)	CV (%)	Mean (%)	CV (%)	Mean (%)	CV (%)
	5·10	17·4	3·80	26·6	4·33	13·7	5·61	32·6
Severn	**Ordovician–Silurian**		**Devonian–Carboniferous–Permian**		**Triassic–Jurassic**		**Suspended sediment**	
	Mean (%)	CV (%)	Mean (%)	CV (%)	Mean (%)	CV (%)	Mean (%)	CV (%)
	3·23	19·9	4·04	13·4	6·87	22·3	3·23	29·4

Table VI. Tracer-specific weightings

Tracer property	Weighting (W_i)
Total P	0·623
Cu	0·664
Dithionite Mn	0·503
Ni	0·140
Cr	0·285
Zn	0·353
Dithionite Al	0·785
Na	0·783
Mg	0·489
K	0·783
Ca	0·415
Pyrophosphate Al	0·568
Pb	0·200
N	0·459
Total of pyrophosphate and dithionite Al	0·929

An organic matter content correction factor O_{g1} is also incorporated into the optimized mixing model, because research has demonstrated that the magnitude of the organic fraction will influence element concentrations (Hirner *et al*., 1990). A correction factor is therefore necessary to make the fingerprint property concentrations associated with the basin outlet suspended sediment samples, and with the source material samples for the geological subareas, more directly comparable. Organic carbon content is used here as a surrogate for organic matter content (Peart and Walling, 1986), and typical values for the study basins are presented in Table V. The correction factor is calculated on the same basis as that used for particle size, yielding mean values of 1·10 (Devonian), 1·47 (Carboniferous) and 1·29 (Permian) for the Exe and 1·00 (Ordovician–Silurian), 0·80 (Devonian–Carboniferous–Permian) and 0·47 (Triassic–Jurassic) for the Severn.

The tracer-specific weighting W_i is used in the optimized mixing model calculations to take account of the differing levels of precision associated with the measurements of individual tracer properties. The use of this factor ensures that the property providing the greatest precision within each composite signature exerts the greatest influence upon the mixing model solutions relating to that signature. W_i is based upon replicate laboratory measurements for each property, and is calculated using the inverse of the square root of the variance associated with each set of replicates (cf. Makas *et al*., 1987). Standardization of the replicate data ensures direct comparability of the values for W_i pertaining to each composite signature. The weightings used in this study are presented in Table VI.

To assess the goodness-of-fit associated with the optimized mixing model, the actual fingerprint property concentrations measured in the basin outlet suspended sediment samples were compared with the corresponding values predicted by the model based on the estimates for the percentage contributions of source material from each geological subarea. The values of relative error provided by this comparison, for each property within each composite signature, were averaged to provide a mean value for each individual suspended sediment sample collected at the basin outlets (see Tables VII and VIII). The mean relative errors are commonly of the order of ±10 per cent, and thereby confirm that the mixing model is able to provide an acceptable prediction of the concentrations of the fingerprint properties associated with individual suspended sediment samples.

Table VII. Mean percentage relative errors for the mixing model calculations for the Exe

Date	Sample point	Mean % error	SE mean
18/12/92		9·6	1.44
26/05/93	1	9·8	1·11
26/05/93	2	8·8	1·87
26/05/93	3	9·9	2·01
11/06/93		9·1	1·66
16/06/93	1	8·5	1·98
16/06/93	2	8·8	2·09
1/10/93		7·1	1·77
6/10/93		10·4	1·28
7/12/93	1	11·0	1·98
7/12/93	2	8·5	1·53
8/12/93	1	8·2	1·33
8/12/93	2	8·8	1·89
8/12/93	3	7·8	1·88
19/12/93	1	10·3	1·51
19/12/93	2	7·9	1·29
19/12/93	3	6·9	1·66
19/12/93	4	10·2	2·00
20/12/93	1	9·1	1·44
20/12/93	2	9·6	1·51
20/12/93	3	7·7	1·78
20/12/93	4	9·6	1·99
20/12/93	5	8·6	1·81
20/12/93	6	8·9	1·52
5/01/04	1	9·5	1·83
5/01/94	2	7·9	1·92
5/01/04	3	8·0	1·84
3/02/94	1	8·6	2·22
3/02/94	2	8·4	1·59
3/02/94	3	9·7	2·11
3/02/94	4	10·7	1·88
3/02/94	5	10·3	2·70
3/02/94	6	9·9	1·72
23/02/94	1	8·4	1·95
23/02/94	2	10·5	1·49
1/04/94	1	8·9	1·77
1/04/94	2	9·6	1·99
1/04/94	3	9·9	1·44
1/04/94	4	7·2	2·02
24/05/94	1	10·6	1·52
24/05/94	2	8·3	1·89
24/05/94	3	7·8	1·52

The sensitivity of the model output to the variability of fingerprint property concentrations associated with source materials from each geological subarea was also tested. This involved repeating the mixing model calculations for an individual sediment sample from each study basin, using ±2 SE of the source material sample means. In each case, changes in the estimates for the relative contributions from each subarea were generally in the order of 3·5 per cent, with a maximum of 5·8 per cent. Despite these changes, sources remained in the same order of importance.

Although the goodness-of-fit data presented above confirm that the model produces a reasonable agreement between simulated and observed fingerprint property concentrations, they cannot directly verify the mixing model results. Validation would require sediment source information provided by alternative techniques, e.g. direct monitoring programmes. Thus, although fingerprinting procedures do provide an alternative approach for sediment source assessment, direct validation of the results produced ultimately relies upon the findings of more traditional methods.

Table VIII. Mean percentage relative errors for the mixing model calculations for the Severn

Date	Sample point	Mean % error	SE mean
1/12/92	1	5·8	3·90
1/12/92	2	6·0	3·84
1/12/92	3	6·5	2·89
1/12/92	4	6·8	3·11
1/12/92	5	7·2	4·50
1/12/92	6	8·1	3·89
1/12/92	7	7·4	4·08
15/01/93	1	10·1	6·00
15/01/93	2	9·8	5·18
15/01/93	3	10·3	3·72
15/01/93	4	10·6	2·93
15/01/93	5	11·0	1·99
15/01/93	6	11·2	4·00
1/10/93		8·5	3·60
28/11/93		7·9	3·88
10/12/93		11·4	4·46
12/12/93		5·8	2·84
28/02/94	1	10·0	2·63
28/02/94	2	9·2	4·70
28/02/94	3	8·4	5·80
1/03/94	1	8·5	5·13
1/03/94	2	10·9	3·22
24/03/94		11·3	4·59

RESULTS AND DISCUSSION

Testing the consistency of the approach using previous findings

Consideration of the mixing model results for the mean and seasonal relative contribution from each distinct geological subarea identified within the Exe and Severn basins can, however, provide a useful means of testing the consistency of the composite fingerprinting approach.

Mean contributions from the subareas. For the sediment load sampled at Thorveton in the Exe, the highest mean contribution is provided by the area underlain by the Carboniferous rocks in the south (57·3 per cent), whilst the lowest is provided by the northern area underlain by Devonian rocks (16·7 per cent). High inputs from the Carboniferous strata are consistent with the steep slopes and highly dissected terrain, the impermeable soils, and the intensive dairy farming with associated poaching, that characterize this area and which would promote relatively high sediment yields. The northern areas of the Exe basin, underlain by Devonian rocks, are characterized by the highest values of annual precipitation and runoff, but the mean suspended sediment contribution from this geological subarea is limited due to the greater resistance of these rocks to erosion (cf. Durrance and Laming, 1982) and the less intensive nature of the agriculture practised in the north (cf. Findlay *et al*., 1984). The central and southern parts of the Exe basin, underlain by Permian rocks, represent the second most important sediment source and provide a mean contribution of 26·0 per cent to the suspended sediment load sampled at Thorverton. Sediment production in areas underlain by Permian rocks is promoted by the increased proportion of land under arable agriculture which is found in these parts of the Exe basin (cf. Findlay *et al*., 1984).

Taking account of the areas of the Exe basin underlain by the three geological systems (i.e. Devonian 48·6 per cent, Carboniferous 40·5 per cent and Permian 10·9 per cent), the relative contributions from these geological areas to the sediment output from the basin indicate that specific sediment yields from the three geological types are in the ratio 1 (Devonian): 4·1 (Carboniferous): 6·9 (Permian). These values are reasonably consistent with estimates of the suspended sediment yields of different subcatchments presented by Walling and Webb (1987), i.e. Upper Exe (Devonian) = 19 t km^{-2} a^{-1}, River Dart (Carboniferous) = 58 t km^{-2} a^{-1} and River Lowman (Permian) = 52 t km^{-2} a^{-1}. Inconsistencies reflect the fact that the geological subareas do not conform perfectly with the subcatchments of the Exe basin. Furthermore, it must also be recognized that the mixing model calculations incorporate no weighting for the relative magnitude of the suspended sediment load associated with each individual flood event sampled. Consequently, the results may not provide an accurate

indication of the contribution of each geological subarea to the longer-term (e.g. annual) suspended sediment load at Thorverton.

For the sediment load sampled at Bewdley in the Severn, the most important contribution (59·8 per cent) is provided by the area underlain by Triassic–Jurassic strata in the east. Sediment production in this area is promoted by the increased erodibility of these sandstones (cf. Hains and Horton, 1969) and the high proportion of arable land use (e.g. 50 per cent of the catchment area of the Tern tributary) which characterizes the eastern areas of the upper and middle Severn basin (cf. Ragg *et al*., 1984). A mean contribution of 32·7 per cent is calculated for the area underlain by Ordovician–Silurian rocks in the west. Sediment production in these western areas is promoted by local very high rainfall intensities, by steep slopes which produce a high-energy fluvial system, by catchment disturbance associated with clearfelling activities in areas of commercial coniferous forest, and by the poaching of surface soils in association with dairy farming (cf. Rudeforth *et al*., 1984). The smallest mean contribution (7·5 per cent) is provided by the area underlain by Devonian–Carboniferous–Permian strata. These rocks occupy the central zones of the upper and middle Severn, where the influence of the environmental conditions which promote increased sediment production in the west and the east is diminished. For example, the high annual preciptiation and extreme precipitation intensities, which are likely to play an important role in sediment generation in the west, decline markedly in the central part of the study basin, and the high proportion of arable land use which promotes sediment production in the east is not found in the areas represented by this particular geological system. Furthermore, the Devonian–Carboniferous–Permian geological system constitutes the smallest proportion of the study catchment and is therefore likely to encompass fewer potential source areas.

Taking account of the mean relative contributions of the three geological subareas of the Severn basin to the sediment load at Bewdley and the proportions of the total catchment area that they occupy (i.e. Ordovician–Silurian 48·7 per cent; Devonian–Carboniferous–Permian 19·6 per cent; Triassic–Jurassic 28·5 per cent), their specific sediment yields are estimated to be in the ratio 1 (Devonian–Carboniferous–Permian): 1·75 (Ordovician–Silurian): 5·48 (Triassic–Jurassic). These values are fairly consistent with existing knowledge of suspended sediment yields from the basin, based on infrequent sediment sampling (R. A. Foster, personal communication), i.e. River Vyrnwy (Devonian–Carboniferous–Permian) = 7·7 t km^{-2} a^{-1}, Upper Severn at Abermule (Ordovician–Silurian) = 25·1 t km^{-2} a^{-1} and River Tern (Triassic–Jurassic) = 58·6 t km^{-2} a^{-1}. However, as with the Exe, the geological subareas do not entirely conform with the major subcatchments, and the fingerprinting values must be treated with caution since they have not been weighted according to the magnitude of the sediment loads at the time of sample collection.

Seasonal variations in the relative contributions from the subareas. To permit an assessment of seasonal variations in the relative contributions from the geological subareas in the upper and middle Exe and Severn basins, floods sampled at the basin outlets were grouped into winter (December, January, February), spring (March, April, May), summer (June, July, August) and autumn (September, October, November) events. The relative contribution from each geological subarea, calculated for the sediment samples collected within each season, were then averaged to provide the mean seasonal contribution from each of the subareas under scrutiny for each study basin. Suspended sediment samples retrieved at Thorveton encompassed all seasons, whilst those from Bewdley encompassed all seasons except summer.

Figure 5 illustrates the seasonal variation of the relative contributions from the three geological subareas in the Exe basin. Contributions from the area underlain by the Devonian strata to the suspended sediment load sampled at Thorverton are greatest (40·0 per cent) during the spring, reflecting the occurrence of several extreme rainfall events in the north of the Exe basin during the spring months of the study period. Sediment contributions from the Permian subarea are greatest during winter and spring, i.e. 35·5 per cent and 25·5 per cent, respectively, when the erosion of bare tilled soils associated with arable cultivation in this subarea during these seasons would be at a maximum. The maximum relative contribution from the areas underlain by Carboniferous rocks during the summer (76·0 per cent) may reflect the increased erosion of both surface soils in pasture areas and channel banks during the summer, associated with the poaching caused by intensive dairy farming (cf. Heathwaite, 1994).

Figure 6 presents the corresponding seasonal results for the Severn basin. In contrast to the Exe, seasonal variations are less clear. Sediment contributions from the area underlain by the Ordovician–Silurian rocks are

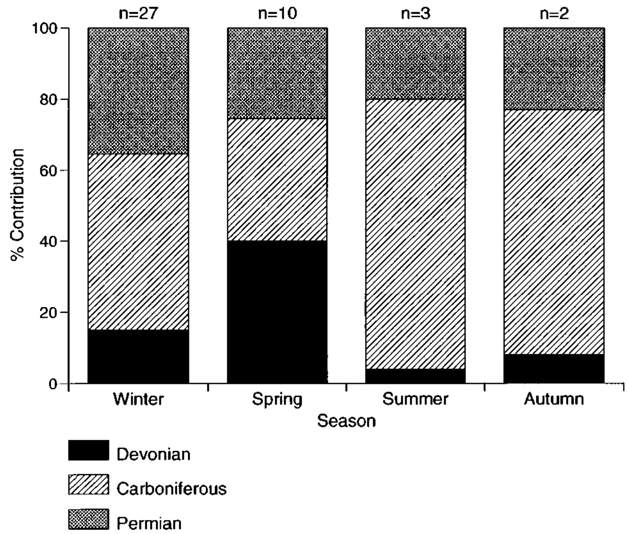

Figure 5. Seasonal variability in the mean relative contributions from each geological subarea in the Exe study basin

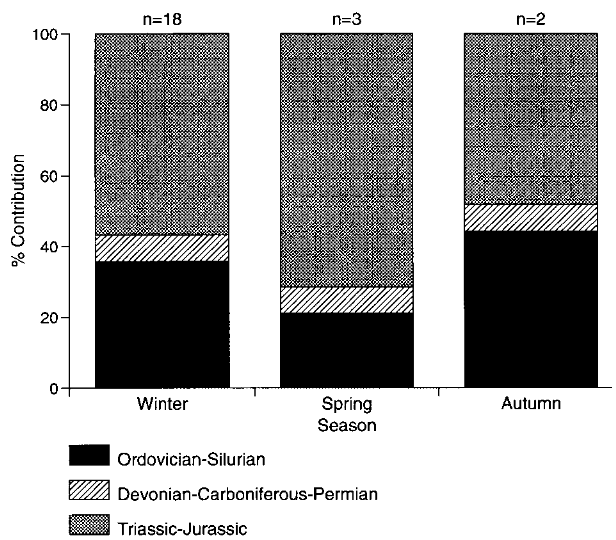

Figure 6. Seasonal variability in the mean relative contributions from each geological subarea in the Severn study basin

higher during the winter and autumn seasons (i.e. 35·8 per cent and 44·2 per cent, respectively); and this could be due to a number of factors, such as the seasonal distribution of high magnitude rainfalls in higher altitude areas or enhanced sediment production associated with forestry activities, e.g. clearfelling, in western areas at these times (cf. Leeks and Roberts, 1987). Contributions from the Triassic–Jurassic subarea are highest during the spring (71·5 per cent), in response to the widespread exposure of bare soils to rainsplash, and erosion by surface runoff associated with extensive spring sowing activities in eastern areas.

Although the seasonal patterns in the relative contributions from the different geological subareas presented above are again consistent with existing knowledge of seasonal variations in erosion processes, it must be recognized that the values obtained will be heavily dependent on the representativeness of the suspended sediment samples collected during the individual seasons.

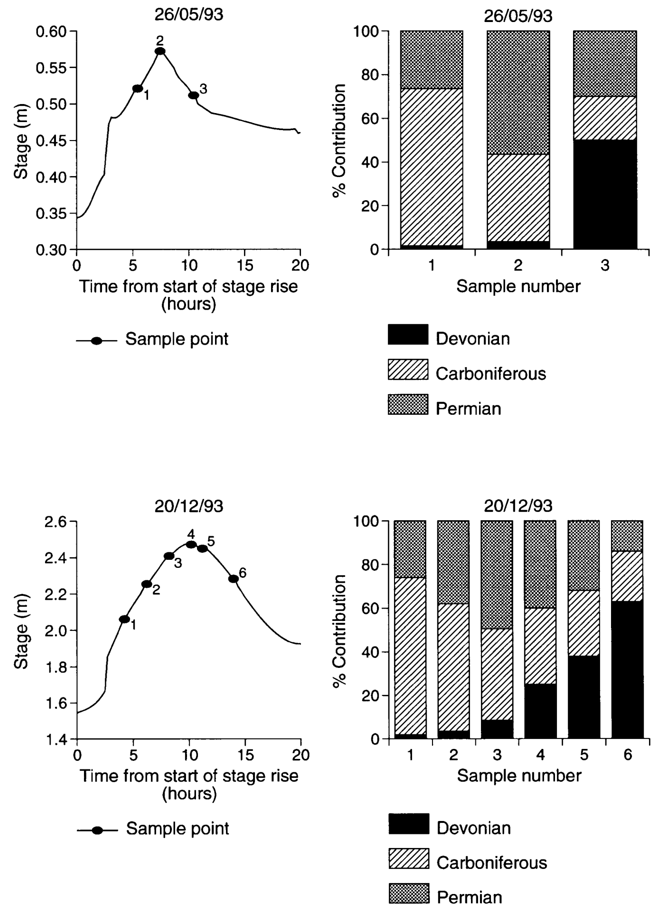

Figure 7. Intra-storm variability in the relative contributions from each geological subarea in the Exe study basin for two selected flood events

Testing the consistency of the approach using alternative lines of evidence

More detailed analysis of the consistency of the results provided by the composite fingerprinting approach is based on a comparison of the results obtained during individual flood events with information on flood behaviour. In this case it is possible to test whether variations in the relative importance of different source areas during a flood event, indicated by the mixing model results, are consistent with information on floodwater travel times and origins.

Flood routing times. Figure 7 presents the results obtained from the mixing model concerning variations in the relative contributions from the geological subareas constituting the Exe basin during two flood events sampled at Thorverton. Both flood events are known to have influenced the entire Exe basin and so provide good examples for comparing the mixing model results with typical floodwater routing times. During the event sampled on 26 May 1993, contributions from the Carboniferous subarea in the south dominate at sample point 1 (72·0 per cent) and progressively decrease as the flood continues to 20·0 per cent at sample point 3 (6 h later). At the same time, the contribution from the Permian subarea, which lies predominantly in the middle portions of the Exe basin, increases from 26·5 per cent at sample point 1 to a maximum of 56·5 per cent at sample point 2 and then decreases again to 30·0 per cent at sample point 3. The contribution from the northern Devonian subarea increases throughout the flood from 1·5 per cent at sample point 1 to 50·0 per cent at sample point 3. Analysis of discharge data for the Exe basin indicated that typical stormwater travel times, from Exmoor in the north to the basin outlet at Thorverton in the south, were of the order of 6–8 h. The intra-storm variation in

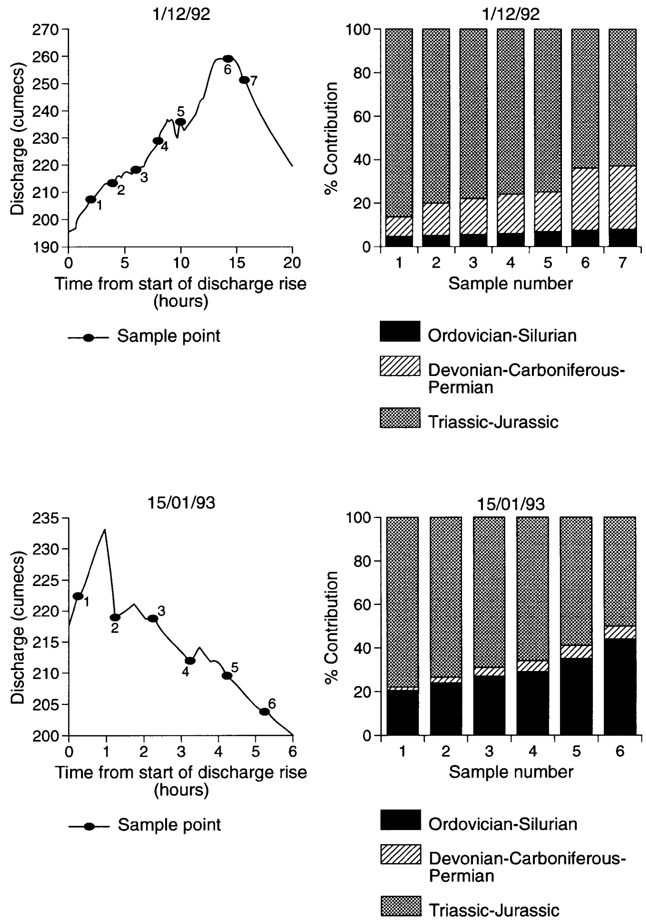

Figure 8. Intra-storm variability in the relative contributions from each geological subarea in the Severn study basin for two selected flood events

source area contributions obtained for the event of 26 May 1993, which demonstrate a predominantly southern spatial provenance in the earlier stages of the flood, moving to a more central and then northern spatial provenance in the later stages, are thus clearly consistent with typical stormwater travel times. The mixing model results for the flood sampled on 20 December 1993 also appear to be compatible with typical stormwater travel times. Sediment contributions from the Carboniferous rocks in the south are highest at sample point 1 (72·0 per cent) and then decrease throughout the flood to a minimum of 23·0 per cent at sample point 6 (11 h later). At the same time, the contribution from the Permian strata increases from 26·0 per cent at sample point 1 to a maximum of 49·5 per cent at sample point 3 and then decreases to a minimum of 14·0 per cent at sample point 6. Devonian strata contributions are low in the earlier stages of the flood, e.g. 2·0 per cent at sample point 1, but increase to 63·0 per cent at sample point 6. These results are again consistent with the gradual arrival of increasing proportions of floodwater from the central and then northern subareas of the Exe basin as the flood event proceeds. This consistency also indicates that the Exe basin is characterized by an efficient fluvial suspended sediment delivery system with limited temporary channel storage and remobilization (cf. Lambert and Walling, 1986, 1988), with the result that the mixing model estimates of intra-storm variations in the spatial provenance of suspended sediment samples collected at Thorverton, directly reflect fluctuations in the contribution of the primary source areas, as opposed to 'averaging' of these inputs as a result of channel storage and remobilization.

Figure 8 examines intra-storm variations in the relative contributions from each geological subarea constituting the Severn basin for two flood events sampled at Bewdley. As with the examples used for the Exe, both flood events were associated with precipitation which encompassed the entire basin and so provide suitable cases for comparing variations in subarea contributions estimated using the mixing model with typical flood routing times. During the flood event of 1 December 1992, the contribution from the Triassic–Jurassic geological subarea in the east dominates at sample point 1 (86·3 per cent) and then decreases as the flood event continues to a minimum of 68·0 per cent at sample point 7 (14 h later). At the same time, the relative contribution from the Devonian–Carboniferous–Permian subarea in the central portions of the Severn basin increases from 9·0 per cent at sample point 1, to a maximum of 29·0 per cent at sample point 7. Contributions from the Ordovician–Silurian geological subarea in the west are low throughout the flood event but increase gradually from 4·7 per cent at sample point 1 to 8·0 per cent at sample point 7. Analysis of stage and discharge data revealed that typical stormwater travel times for the upper and middle Severn are 1·5–3 days. These results suggest that the contribution from the geological subareas closest to the basin outlet at Bewdley (i.e. the Triassic–Jurassic strata) dominates in the early stages of the flood, but decreases in relative importance as increasing volumes of sediment and floodwater successively arrive from the central and then the western portions of the basin as the flood continues. However, the contributions from the central and western areas of the basin, in particular, arrive sooner than might be expected according to typical routing times, as the sediment sampling undertaken during this flood encompassed only 14 h. Similar results are observed for the flood event sampled on 15 January 1993. The contribution from the geological subarea closest to the basin outlet at Bewdley (i.e. the Triassic–Jurassic strata) is again dominant at sample point 1 (78·0 per cent), and decreases as the flood event continues to a minimum of 50·0 per cent at sample point 6 (5 h later). However, the contributions from the Ordovician–Silurian geological subarea in the west are reasonably high throughout the flood event, e.g. 20·5 per cent at sample point 1 and increasing to 44·0 per cent at sample point 6. These mixing model estimates are clearly not entirely compatible with typical floodwater routing times, as a significant contribution of sediment apparently arrives from western areas after only 5 h.

It seems likely, therefore, that the intra-storm variations in spatial provenance for the suspended sediment load sampled at Bewdley described above, reflect, at least in part, the role of storage and remobilization phenomena in producing sediment signature 'averaging' (cf. Klages and Hsieh, 1975; Johnsson and Meade, 1990). Consequently, the mixing model results represent both primary and secondary source contributions during these two flood events. Temporal discontinuities could be expected to be more apparent in the fluvial suspended sediment delivery system of a larger-scale basin such as the upper and middle Severn, where the greater drainage areas, longer transportation distances and larger channels provide more opportunities for sediment deposition and subsequent remobilization (cf. Trimble, 1975, 1977; Meade, 1982; Walling, 1983, 1988). Brown (1987) estimates that during the Holocene, as much sediment was stored within as was transported out of the Severn basin. However, canalization, channelization and general regulation have helped to prevent the remobilization of such sediment from longer-term sinks such as floodplain and backswamp environments. Within-channel stores are therefore likely to be the principal shorter-term sources of remobilized sediment within this particular basin (cf. Thorne and Lewin, 1979; Bull *et al*., 1995). The importance of sediment remobilized from within-channel stores has also been noted in other large drainage basins, e.g. the Mississippi (Meade and Parker, 1985), the Lower Amazon (Meade *et al*., 1985) and the Potomac (Miller and Shoemaker, 1986). The results for the Severn basin emphasize the need for further investigations into typical residence times for fluvial suspended sediment and into the effect of sediment storage and remobilization upon the utility of sediment fingerprinting procedures in larger drainage basins.

Spatial distribution of precipitation. The consistency of the composite fingerprinting approach can be further tested by comparing the mixing model estimates of variations in the spatial provenance of the sampled suspended sediment load with a crude assessment of storm origin based upon catchment precipitation records. In a situation where storage and remobilization phenomena are significant, any mixing model estimates for spatial provenance will not closely resemble the inferred storm origin.

Analysis of rain-gauge data for the Exe basin study area (see location of rain-gauges in Figure 1) for the storm event that occurred on 26 May 1993 indicated that southern areas (e.g. 35·5 mm at the Bickleigh Dorweeke rain-gauge in the Dart tributary sub-basin), central areas (e.g. 25·5 mm at the Huntsham rain-gauge in the Lowman

tributary sub-basin) and northern areas (e.g. 21·5 mm at the Honeymeade rain-gauge in the Barle tributary sub-basin) all received precipitation. Consequently, the mixing model estimates which demonstrate sediment contributions from southern, central and northern geological subareas during this event are compatible with storm origin. Similarly, the mixing model estimates for the flood event on 20 December 1993, which indicate sediment contributions from southern, central and northern areas of the Exe basin, appear to be compatible with the fact that the entire basin received rainfall during this event (e.g. 45·0 mm at the Bickleigh Dorweeke rain-gauge, 35·0 mm at the Huntsham rain-gauge and 30·5 mm at the Honeymeade rain-gauge). Therefore, the fingerprinting results for the Exe basin are consistent with inferences concerning storm origin based on precipitation records.

Analysis of rain-gauge data from the Severn basin (see location of rain-gauges in Figure 3) for the event of 1 December 1992 indicated that western areas received significantly more precipitation (e.g. 64·0 mm at the Moel Cynnedd rain-gauge in the Plynlimon sub-basin) than central (e.g. 20·0 mm at the Llanfyllin rain-gauge in the Perry tributary) and eastern areas (e.g. 13·0 mm at the Childs Ercall rain-gauge in the Tern tributary sub-basin). However, the mixing model estimates cover only 14 h and do demonstrate the early arrival of sediment from the eastern areas closer to the basin outlet, followed by the gradual arrival of increasing proportions of sediment from central and then western areas. Therefore, the fingerprinting results for this flood appear to be compatible with storm origin. Similary, the mixing model estimates for the flood event on 15 January 1993 demonstrate contributions of sediment from all three geological subareas of the Severn basin, which appears to be compatible with the fact that the entire basin experienced some precipitation (e.g. 27·5 mm at the Moel Cynnedd rain-gauge, 19·5 mm at the Llandyllin rain-gauge and 17·5 mm at the Childs Ercall rain-gauge). However, such comparisons between mixing model calculations and precipitation records alone may be inconclusive unless flood events are selected which are the result of precipitation over a particular subarea of the basin in question as opposed to the entire extent of that basin. Further work to document the sediment response of such events is clearly required.

CONCLUSIONS

By studying two different drainage basins of contrasting size and physiographic characteristics, this study aimed to provide a test of the extent to which the composite fingerprinting approach can be successfully utilized to assess the spatial origin of contemporary suspended sediment transported through larger river basins. The mixing model estimates are clearly consistent with existing information regarding the suspended sediment yields from different subcatchments within the study basins and current knowledge concerning seasonal variations in land use and associated erosion processes. However, a degree of caution is necessary because the variability associated with source material fingerprint property concentrations is not explicitly incorporated into the mixing model calculations, and because the mixing model estimates are not weighted according to the magnitude of the suspended sediment load transported at the time of sample collection. Detailed analysis using a comparison of intra-storm results with typical flood routing times and storm origin (precipitation data) also confirms the consistency of the composite fingerprinting approach. However, in the case of the Severn basin, the role of storage and remobilization in producing signature 'averaging' may complicate comparison of the fingerprinting data with typical floodwater routing times and a comparison with precipitation data alone may be potentially misleading. As storage and remobilization phenomena have consistently been identified in large (>500 km^2) drainage basins in North and South America (Meade, 1982; Meade *et al*., 1985), western Europe (Brown, 1987; Macklin and Klimek, 1992) and Australia (Olive and Rieger, 1986), the usefulness of employing, and the interpretation of the results provided by fingerprinting procedures in such basins must be further assessed.

Fingerprinting procedures based on a simple qualitative interpretation of single-component signatures such as colour (e.g. Grimshaw and Lewin, 1980) must be seen as attractive in terms of their simplicity. However, although a quantitative composite-signature approach is more demanding in terms of laboratory analysis and statistical testing, it affords more reliable source discrimination by reducing the likelihood of spurious source–sediment matches. Perhaps the greatest problem compromising the cost–benefit of the fingerprinting approach is that direct validation of the results is largely dependent upon the existence of previous investigations within

study catchments using more traditional methods. If, however, the validity of the approach is accepted, it affords a means of assessing sediment provenance without the need for detailed monitoring at a large number of sites. Source material characterization can be based on a short intensive survey, and bulk suspended sediment samples then need to be collected at the basin outlet during major storm events.

If the value of the fingerprinting approach as a tool for investigating sediment provenance in larger-scale river basins is to be fully realized, scope undoubtedly exists for further development. Such development could address the following points.

(a) The fingerprinting of spatial provenance is best suited to heterogeneous basins such as the Exe and Severn, where contrasting geological types contribute sediment characterized by distinctive composite signatures. Further work is clearly required to assess the applicability of spatial provenance fingerprinting to source area investigations in more homogeneous basins, and hence the degree of heterogeneity necessary before the suite of properties constituting the composite signatures required to distinguish spatial sources becomes unmanageable and unrealistic.
(b) Although this study has focused on the assessment of spatial origin, future research should investigate the possibility of obtaining information on both spatial provenance and source type for larger catchments. Walling and Woodward (1995) have already confirmed this potential using a medium-scale (276 km^2) study basin.
(c) The variability of fingerprint property concentrations for different sources should be included in mixing model calculations to enable the provision of confidence limits for the estimates of the relative contributions from each potential source.
(d) It may be desirable to restrict laboratory analysis of fingerprint properties to discrete particle-size classes, to avoid the uncertainties associated with compensating for contrasts in particle size and organic matter content between catchment source and suspended sediment samples using correction factors.
(e) The reliability of the discrimination afforded by composite signatures could be further improved with the inclusion of additional parameters, preferably with differing environmental behaviour to those already employed.
(f) Fingerprint properties used in the mixing model could be further weighted according to their susceptibility to geochemical transformation during the stages of erosion, transportation and deposition interposed between drainage basin source area and outlet.
(g) Guidelines based on a range of basin property statistics could be developed to rationalize initial listings of fingerprint properties, thereby ensuring efficient use of field and analytical resources.
(h) The extent to which signature ‘averaging’ influences the results provided by sediment fingerprinting studies undertaken in larger drainage basins requires further investigation.
(i) The representativeness of mixing model results for mean sediment provenance could be improved by deriving load-weighted estimates which take account of the proportion of the total sediment loading transported during individual flood events.

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